Journal of Sol-Gel Science and Technology 26, 827–830, 2003
© 2003 Kluwer Academic Publishers. Manufactured in The Netherlands.

Nucleation Phenomenon in Silica Xerogels and Pd/SiO_2, Ag/SiO_2, Cu/SiO_2 Cogelled Catalysts

CHRISTELLE ALIÉ*, STÉPHANIE LAMBERT, BENOÎT HEINRICHS AND JEAN-PAUL PIRARD
Laboratoire de Génie Chimique, B6a, Université de Liège, B-4000 Liège, Belgium
c.alie@ulg.ac.be

Abstract. Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 xerogel catalysts have been synthesized by cogelation of tetraethoxysilane (TEOS) and chelates of Pd, Ag and Cu with 3-(2-aminoethylamino)propyltrimethoxysilane (EDAS). It appears that, in cogelled samples, the metal complex acts as a nucleation agent in the formation of silica particles. The resulting catalysts are then composed of completely accessible metallic crystallites with a diameter of about 3 nm located inside silica porous particles with a monodisperse microporous distribution. Xerogels without metal synthesized with EDAS and TEOS (C. Alié, R. Pirard, A.J. Lecloux, and J.-P. Pirard, J. Non-Cryst. Solids **289**, 88 (2001)) verify this hypothesis of nucleation by EDAS.

Keywords: sol-gel process, low-density xerogel, cogelled catalysts, nucleation, metal dispersion

1. Introduction

In order to homogeneously disperse nanometer-sized metal particles in a silica matrix, Breitscheidel et al. [1] prepared modified xerogels by using organically substituted alkoxydes of the type $RSi(OR')_3$ (additive) where R contains a ligand able to form a chelate with a metal ion such as Pd^{2+}, Pt^{2+}, or Ni^{2+}. This ligand is linked to the hydrolysable silyl group $-Si(OR')$ by an inert spacer such as $-(CH_2)_3-$. Heinrichs et al. [2] developed this cogelation method for the preparation of Pd/SiO_2 aerogel catalysts by using an alkoxyde with a ligand complexing palladium. The resulting catalysts are composed of completely accessible palladium crystallites located inside silica particles. It was shown that these samples are sinterproof during supercritical drying due to the fact that Pd crystallites cannot migrate because they are trapped inside the microporous SiO_2 particles. Alié et al. [3] prepared low-density xerogels by incorporation of an additive $RSi(OR')_3$ prior to gelation. When the additive contains methoxy groups, it reacts first to form nuclei on which the main silica precursor which contains ethoxy groups condenses to form silica particles. This nucleation mechanism occurs only when a large difference in reactivity between additive and silica precursor exists.

The main purpose of this study is to synthesize Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 xerogel catalysts with a high metal dispersion. In this study, the main silica precursor is tetraethoxysilane = $Si(OC_2H_5)_4$ (TEOS), the additive with ligand complexing metal is 3-(2-aminoethylamino)propyltrimethoxysilane = NH_2-CH_2-CH_2-NH-$(CH_2)_3$-$Si(OCH_3)_3$ (EDAS), and the metal precursor is either Pd acetylacetonate = $Pd[CH_3COCH{=}C(O-)CH_3]_2$ ($Pd(acac)_2$), Ag acetate = $Ag[CH_3CO(O-)]$ ($Ag(OAc)$) or Cu acetate = $Cu[CH_3CO(O-)]_2$ ($Cu(OAc)_2$). The nucleation phenomenon by the metal complex in the formation of silica particles is examined as well as the localization and accessibility of Pd, Ag and Cu in cogelled catalysts.

2. Experimental

2.1. Sample Synthesis

Five Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 catalysts were prepared from TEOS, EDAS, H_2O, ethanol and NH_3.

*To whom all correspondence should be addressed.

Table 1. Synthesis operating variables and sample textural properties.

Catalyst	$Pd(acac)_2$ (m mol)	EDAS (m mol)	TEOS (mol)	EDAS/TEOS	Pd (wt%)	Gel time (min)	S_{BET} (m^2/g)	V_v (cm^3/g)	d_p (nm)
Pd1	1.074	2.15	0.186	0.0115	1.11	30	365	3.2	18.5
Pd2	1.369	2.74	0.186	0.0147	1.57	28	370	2.8	17.9
Pd3	1.835	3.62	0.185	0.0195	2.45	26	475	2.6	15.1
Pd4	2.289	4.58	0.184	0.0249	3.07	26	495	2.5	12.6
Pd5	4.811	9.62	0.179	0.0537	4.52	22	570	2.0	9.8

S_{BET}: specific surface area obtained by BET method; V_v: total pore volume; d_p silica particle diameter measured by TEM.

For the need of concision, the following steps are explained with Pd/SiO_2 catalysts only. $Pd(acac)_2$ powder and EDAS were mixed together in 55 ml of ethanol (the molar ratio of EDAS/$Pd(acac)_2 = 2$). The slurry was stirred at room temperature until a clear yellow solution was obtained (about half an hour). After addition of TEOS, a solution of aqueous 0.18 N NH_3 in 55 ml of ethanol was added to the mixture under vigorous stirring. The vessel was then closed and heated to 70°C for 3 days (gelling and aging). As shown in Table 1, five Pd/SiO_2 catalysts with various EDAS/TEOS molar ratio and thus various weight percentages of palladium have been prepared.

The wet gels were then dried under vacuum according to the following procedure: the flasks were opened and put into a drying oven heated to 60°C, and the pressure was slowly decreased to the minimum value of 1200 Pa after 90 h. The drying oven was then heated at 150°C for 72 h. All the catalysts were calcined in a flow of dry air (9 Nl/h) at 400°C for 12 h and subsequently reduced under flowing H_2 (20 Nl/h) at 350°C for 3 h.

2.2. *Catalyst Characterization*

Skeletal densities were measured by He pycnometry. N_2 adsorption-desorption isotherms at 77 K and mercury porosimetry experiments were carried out. All the samples were examined using a transmission electron microscope to obtain particle sizes. The different procedures are described in [2]. CO chemisorption measurements were also carried out on the Pd/SiO_2 catalysts.

3. Results

The silica particle sizes d_p have been evaluated by visual measurement on a series of particles observed by TEM. The silica particle size decreases from 18 to 10 nm as the EDAS/TEOS ratio increases (Table 1).

All xerogel catalysts have a non-classical behaviour when submitted to mercury porosimetry [2, 4, 5]: at low pressure, the sample collapses under mercury pressure and above a pressure of transition P_t, mercury can enter into the network of small pores not destroyed during the compression at low pressure. It has been shown that during compaction, the isostatic mercury pressure P completely crushes pores of size larger than a limit size L and leaves the pores of smaller size unchanged [5]. The relation between L and P is given by Euler's law for the buckling of a cubic structure: $L = k/P^{\sim 0.25}$, where k is a function of the elastic modulus of the mineral oxide filaments E and the diameter of the filaments d [5]. The k value, which can be different for each sample, allows the determination of the pore volume distribution in relation to the pore size. In fact, at P_t, both equations, the buckling law and Washburn's law $L = -4\sigma \cos\theta / P$ (where σ is the surface tension of mercury and θ is the angle of contact between the solid and mercury) $\cong 1500/P$ (if P is expressed in MPa and L in nm) are valid and k is given by the relationship $k = 1500/P_t^{0.75}$. Figure 1 shows the relation existing between k and the

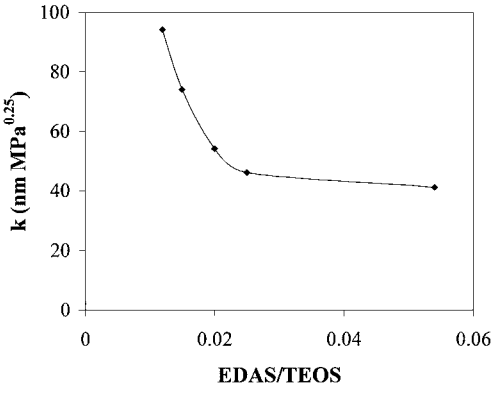

Figure 1. Buckling model constant k versus EDAS/TEOS for Pd/SiO_2 samples.

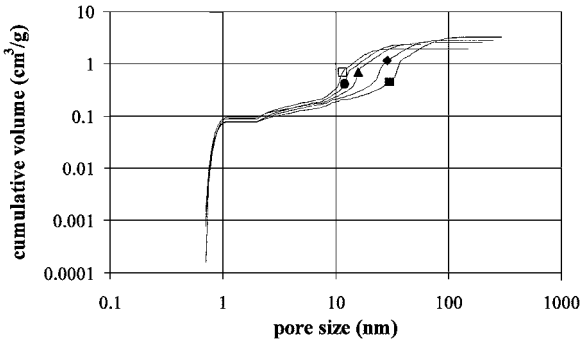

Figure 2. Pore size distributions as a function of the ratio EDAS/TEOS for Pd/SiO_2 samples with EDAS/TEOS ratio = 0.0115 (■), 0.0147 (♦), 0.0195 (▲), 0.0249 (●) and 0.0537 (□).

ratio of EDAS/TEOS: the higher the EDAS content, the lower the value of k. In Table 1, it is observed that the higher the EDAS content, the lower the silica particle diameter. So, k decreases with the silica particle diameter. From its definition, a lower value of k means that filaments forming the network of the gel are more fragile when the EDAS content increases [2].

Figure 2 shows the evolution of the cumulative volume distributions over the entire pore size range as a function of the ratio EDAS/TEOS. They were obtained by applying the method proposed by Alié et al. [3]. All the catalysts contain micropores, mesopores and macropores. The distribution shifts towards the smaller pores from Pd1 to Pd5 for which the amount of EDAS increases. The pore volume V_v decreases while the surface area S_{BET} increases, respectively from 3.2 to 2.0 cm^3/g and from 365 to 570 m^2/g when the molar ratio of EDAS/TEOS increases from 0.0115 to 0.0537. The pore volume considered here is the total pore volume V_v which takes into account the volume of all pores.

4. Discussion

TEM micrographs obtained for the Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 catalysts show metallic particles located inside microporous silica particles. This suggests that the localization of the metal inside the silica matrix was induced by a nucleation process initiated by the ligand of the metal, namely EDAS. Due to the hydrolysable functions of EDAS, Si—O—Si bonds can form all around the additive. Alié et al. showed that the linear relation describing the mechanism of nucleation by an additive is the following [3]

$$d_p^3 = C([\text{additive}] + [\text{main silica precursor}])/[\text{additive}] \quad (1)$$

where d_p is the diameter of SiO_2 particles, C is a constant and [additive] and [main silica precursor] are the amount of additive and main silica precursor in the gel. For Pd/SiO_2 catalysts and EDAS-TEOS samples without metal [3], a nearly linear relation passing through the origin is obtained (Fig. 3). For AES-TEOS samples without metal [3] (AES = 3-aminopropyltriethoxysilane), d_p^3 is independant of the variable ([additive] + [main silica precursor])/[additive]. For all the samples synthesized with EDAS, methoxy groups contained in EDAS react faster than ethoxy groups contained in TEOS. This indicates that the nucleation mechanism by EDAS takes place in case of TEOS as main silica precursor. On the contrary, in case of both ethoxy groups (series AES-TEOS) for main silica precursor and additive, d_p^3 remains nearly constant (Fig. 3). This is the reason why it can be considered that there is no nucleation mechanism by the additive in this case.

A very important concern about cogelled catalysts is the accessibility of the active centers. Because Pd, Ag and Cu are located inside silica particles, there is a risk that metal particles might not be accessible. The measured activity of Pd/SiO_2 catalysts for ethylene hydrogenation and of Ag/SiO_2 and Cu/SiO_2 catalysts for VOC (Volatile Organic Compounds) removal reaction prove that Pd, Ag and Cu particles are indeed accessible. Furthermore, the agreement between TEM

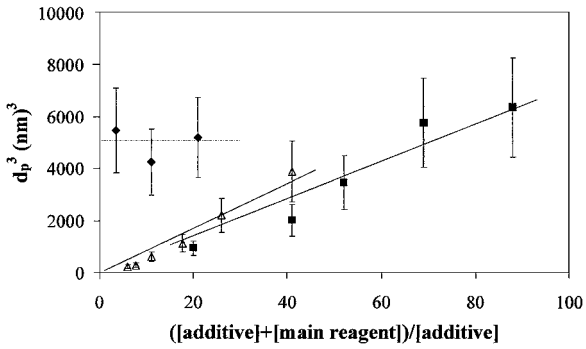

Figure 3. Nucleation of the silica particles by the additive in case of methoxy groups on the additive and TEOS as main reagent (■: Pd/SiO_2 catalysts and Δ: EDAS-TEOS samples without metal) and absence of nucleation mechanism by the additive in case of both ethoxy groups (♦: AES-TEOS samples without metal).

and CO chemisorption results is, for Pd/SiO_2 catalysts, the proof that Pd particles are accessible also to CO molecules.

5. Conclusions

The examination of texture, metal dispersion, and metallites localization in cogelled samples leads to the following conclusion: metallic crystallites with a diameter of about 3 nm are located inside particles exhibiting a monodisperse microporous distribution centered on a pore size of about 0.8 nm. The continuous meso- and macropore distribution is located in voids between these particles and between aggregates constituted of these particles. Although metallic particles are located inside SiO_2 particles, their complete accessibility, via the micropore network, has been demonstrated and these xerogel catalysts have remarkable mass-transfer properties [6]. Finally, because they are larger than the micropores of the silica particles in which they are located, the metallic crystallites in cogelled samples are trapped and are then unable to migrate. In consequence, those catalysts are sinterproof during calcination and reduction steps.

Acknowledgment

C. Alié and S. Lambert are grateful to the Belgian Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture, F.R.I.A, for a PhD grant.

References

1. B. Breitscheidel, J. Zieder, and U. Schubert, Chem. Mater. **3**, 559 (1991).
2. B. Heinrichs, F. Noville, and J.-P. Pirard, J. Catal. **170**, 366 (1997).
3. C. Alié, R. Pirard, A.J. Lecloux, and J.-P. Pirard, J. Non-Cryst. Solids **289**, 88 (2001).
4. C. Alié, R. Pirard, and J.-P. Pirard, J. Coll. Surf. **187/188**, 367 (2001).
5. R. Pirard, S. Blacher, F. Brouers, and J.-P. Pirard, J. Mater. Res. **10**, 2114 (1995).
6. B. Heinrichs, J.-P. Schoebrechts, and J.-P. Pirard, AIChE J. **47**, 1866 (2001).